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(54) Abstract Title  
**Modified lyocell fibre and method of its formation**

(57) A modified lyocell fibre contains elongated domains of polyester, the domains having an aspect ratio of at least 1.5 and being aligned substantially parallel to the axis of the fibre. Modified lyocell fibre or film is prepared by extruding a solution of cellulose in amine oxide through a spinneret (to form fibres) or die (to form films) at an elevated temperature via an air gap where the cellulose solution contains 0.1-60% (based on cellulose) of a thermoplastic low-melting polymer. The cellulose solution containing the low-melting polymer may also form one component of a bicomponent fibre (eg sheath/core or side-by-side fibre), the other component being unmodified lyocell or a polyester.

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Fibre, Film and its Production

This invention relates to modified lyocell fibre and film and to a process for the preparation of modified lyocell fibre or film. "Fibre" is used in this specification to include continuous filament yarns, tows of yarn for cutting into staple fibre and also staple fibre formed from such a tow.

Lyocell fibre and film is produced by dissolving cellulose in a suitable solvent, such as tertiary amine N-oxide mixed with water. A suitable method of manufacture is described in US-A-4,416,698. The solution of cellulose in an amine oxide solvent, which is solid at ambient temperature, is extruded at a temperature of 95-125°C from a spinneret or film die through an air gap into a precipitation bath of water or dilute aqueous amine oxide, and the amine oxide solvent leaches into the bath, producing cellulose fibre or film.

JP-A-8-170224 discloses a biconstituent fibre of the islands-in-the-sea type in which the continuous "sea" component is a cellulose-type polymer spun from an organic solvent system and the "islands" are composed of a polymer dyeable by a disperse dye and are 0.01-3µm in size and form 2-45% by weight of the fibre. The disperse dyeable polymer is for example a polyester such as polyethylene terephthalate, sulphonic acid-modified polyethylene terephthalate or polybutylene terephthalate.

GB-A-2121069 discloses cellulose-based (viscose rayon) fibres for the production of nonwovens containing as mineral fillers barium sulphate, talcum, muskovite, or a mixture thereof, in an amount of from 15 to 60%, preferably 40 to 50%, of the total fibre mass, and, if desired, additionally hydrophobic, polymer or oligomer substances, such as polyethylene, polypropylene, polystyrene, polyacrylic acid ester, polyester, polytetrafluorethylene or waxes, in an

amount of from 1 to 60%, preferably 25 to 50%, of the total fibre mass. GB-A-2008126 discloses the use of polystyrene as a delustrant for viscose rayon fibres.

5           A process according to the invention for the preparation of lyocell fibre or film by extruding a solution of cellulose in amine oxide through a spinneret or film die at elevated temperature via an air gap into an aqueous precipitation bath is characterised in that 0.1-60 wt%  
10           based on cellulose of a thermoplastic low-melting polymer is incorporated into the cellulose solution, the low-melting polymer having a melting point above 25°C but below the extrusion temperature of the cellulose solution.

15           In the process of the invention, the thermoplastic low-melting polymer is in a melted state in the cellulose solution at the extrusion temperature and the melted polymer is aligned in the axial direction of the fibre or film as the solution is extruded. When fibre is extruded through a  
20           spinneret, the low-melting polymer generally forms particles or domains of aspect ratio at least 1.5 and usually at least 2 in the fibre.

          The thermoplastic low-melting polymer should generally  
25           be sufficiently compatible with the cellulose solution that the polymer when molten does not agglomerate as a separate phase from the cellulose solution, but it is preferably not soluble either in amine oxide or in the solution of cellulose. One type of preferred low-melting polymer is a  
30           polyester. Thus, according to another aspect of the invention lyocell fibre is characterised in that the fibre contains elongated polyester domains of aspect ratio at least 1.5, the polyester domains being aligned substantially parallel to the axis of the fibre.

35           In general, we believe that the presence of carboxylic acid groups in the low-melting polymer is advantageous in giving the right degree of compatibility with the cellulose

5 solution. The polymer preferably has an acid value of at least 10, up to for example 50 or 100. We also believe that a branched polymer structure may be advantageous. The melting point of the low-melting polymer is preferably at least 35°C and up to 125°C, most preferably in the range 50 to 100°C, as measured by differential thermal analysis. The Tg of the polymer is preferably higher than 30°C. Examples of polyesters of this type having the required low melting point are formed from a mixture of aromatic dicarboxylic acids selected from isophthalic acid, terephthalic acid, and phthalic acid or anhydride, optionally with an aliphatic dicarboxylic acid such as adipic, succinic or sebacic acid, and one or more aliphatic diols such as neopentyl glycol, ethylene glycol, propylene glycol, propane-1,3-diol, butane-1,4-diol, butylene glycol or diethylene glycol. Branching can be introduced by a trifunctional reagent, for example trimellitic acid or anhydride or trimethylolpropane, glycerol or pentaerythritol. The required acid value can be obtained by using an appropriate excess of carboxylic acid-functional reagent. Such polyesters are sold for use in thermosetting powder coatings, for example under the Trade Marks "Alftalat 03258", "Uralac P2980" or "Grilesta V76-12".

25 Alternative thermoplastic low-melting polymers are polyamides, for example polyamides formed from fatty acid dimers and aliphatic diamines, or olefin copolymers such as ethylene/vinyl acetate or ethylene/butylene/butyl acrylate copolymers, preferably containing a small amount of acrylic acid comonomer to give the preferred acid value.

30 The concentration of cellulose in the solution to be extruded (otherwise known as the spinning solution) is generally 12 to 20% by weight, preferably at least 14 or 15% up to 17 or 18% by weight. We have found that the thermoplastic low-melting polymer tends to reduce the viscosity and shear resistance of the spinning solution, as evidenced by reduction in back-pressure during spinning, so that the concentration of cellulose can be increased

compared to extrusion (spinning) without added polymer. The spinning solution preferably contains water, usually in the range 5-15% by weight, with the remainder being amine oxide.

5           The low-melting polymer can be added to the cellulose solution at any of various points during its preparation. The polymer can for example be premixed with cellulose pulp, the pulp then being mixed with amine oxide and water to form the spinning solution. The polymer can alternatively be  
10           added, preferably in molten form, to a preformed cellulose solution. In a further alternative, a relatively high proportion of low-melting polymer is premixed with cellulose pulp, for example forming 10 to 50% by weight of the mixture. The pulp is then mixed with amine oxide and water  
15           to form a solution which is used as a masterbatch to add the low-melting polymer to the cellulose solution at the required level.

          The cellulose solution containing a low-melting polymer  
20           can be extruded to form fibres using the same spinneret, or to form film using the same extrusion die, at the same temperature as is conventionally used for forming lyocell fibre or film. It can be used as one component of a  
25           bicomponent fibre such as a sheath/core or side-by-side bicomponent fibre, for example it can be used with unmodified lyocell as the other component or with polyester as the other component (particularly when the low-melting polymer is a polyester). Some of the benefits of the present invention may be achieved by spinning lyocell and  
30           the low-melting polymer as a bicomponent fibre, and special dyeing effects may be obtained from a bicomponent fibre having a lyocell sheath and a disperse dyeable polyester core.

35           The domains or particles of low-melting polymer are distributed uniformly throughout the fibre or film as a separate phase. When a carboxy-functional polyester is included in a lyocell spinning solution, for example, the

polyester phase appears as particles or domains of length 70 to 1000 nanometres (nm) and diameter 30 to 400 nm. The polyester phase cannot usually be seen by optical microscopy but can be seen by electron microscopy at x9000 enlargement.

5 Fibre inspection by electron microscope in cross-section shows apparently spherical particles but a longitudinal view shows that the polyester domains are elliptical. The polyester domains generally have an aspect ratio (ratio of length to diameter) of at least 1.5, usually between 2 and

10 4.

The level of low-melting polymer present in the fibre is generally 0.1 up to 30 or even 50 or 60% by weight based on cellulose. The presence of the elongated particles or

15 domains of low-melting polymer gives rise to various effects depending on the concentration of low-melting polymer and on the type of low-melting polymer used.

If the low-melting polymer is used at concentrations of at least 3% by weight based on cellulose, up to 60%, for

20 example 4 to 12%, lyocell fibres having an increased tendency to fibrillation are produced. Such fibres are desirable for use in many non-woven processes, for example wet laying or dry laying on papermaking machinery or

25 hydroentanglement, since they give increased inter-fibre bonding (mechanical entanglement) and hence a paper or nonwoven fabric of increased strength, and also for use in filters.

Fibre or film containing 0.1 to 3 wt% of the low-melting polymer, particularly polyester, has been found to show improved dimensional stability compared to unmodified

30 lyocell fibre and when formed into fabrics, particularly woven fabrics, to have improved crease resistance compared to fabrics of unmodified lyocell fibre.

35

When polyester is used as the low-melting polymer, the fibre or film produced is dyeable with disperse dyes. Levels

of polyester as low as 0.1% by weight, for example 0.25 to 1.0% by weight, can be used as a tracer which is revealed on disperse dyeing, for example with Planil Blue BGFN, without affecting other properties of the lyocell fibre. Fibre or film containing above 1%, preferably above 2%, by weight, polyester can be disperse dyed to produce reasonably deep shades, and film or fabric formed from the fibre can be transfer printed with disperse dyes. A marl effect is possible by blending standard lyocell fibres with the fibres of the invention.

The fibre containing low-melting polymer, particularly polyester, has self-lubricating properties so that it can be processed, for example staple fibre can be carded, without addition of any lubricant finish. The static friction between fibres is low and the dynamic friction is high, giving good web/sliver cohesion. This effect is achieved at levels of 0.3% by weight and above, up to for example 5%. The preferred level of polyester to achieve this self-lubricating effect is 0.4 to 2%. The fibre also retains a permanent soft handle and may have improved crimp retention. Fabrics containing the fibre have improved crease recovery.

The low-melting polymer may be included in lyocell fibre simply for its ability to reduce spinning solution viscosity and shear resistance, allowing spinning of solutions of increased cellulose content. This has advantages of increased throughput and reduced handling of amine oxide solvent per amount of fibre produced. The weight ratio of amine oxide to cellulose in the spinning solution can for example be reduced from 5.0 to 4.5 or below.

The fibre or film can be post-treated with a crosslinker for the low-melting polymer if the low-melting polymer is intended to give a permanent effect and there is a risk of its being removed from the fibre in use, for example by heating or hydrolysis. A carboxy-functional polymer can for example be treated with a crosslinking agent

having epoxide groups or activated hydroxyl groups.

5 Lyocell fibre is spun through an air gap into an precipitation aqueous (spin) bath into which the amine oxide leaches. For the lyocell production process to be economically and environmentally sound, the amine oxide needs to be recovered from the spin bath and recycled. We have found that the low-melting polymer, particularly the polyester described above, does not leach out of the fibre  
10 into the spin bath and causes substantially no contamination of the spin bath or of the recycled amine oxide.

The invention is illustrated by the following Examples, in which parts and percentages and ratios are by weight.

15

Example 1

Wood pulp was mixed at 100°C for 5 minutes in a Z-blade mixer with a 3:1 amine oxide:water solution. "Alftalat  
20 03258" carboxy-terminated saturated polyester resin available from Hoechst AG was added to the mixture at a level of 2.0% based on wood pulp. Mixing was carried out for a further 5 minutes at ambient pressure before vacuum was applied, gradually removing water from the mixture while  
25 mixing until a solution comprising 15.0% cellulose, 0.3% polyester, 74.7% amine oxide (N-methyl morpholine oxide) and 10.0% water was formed. This spinning dope was solidified by cooling (its melting point was about 60°C), chipped and spun into fibre using an extruder feeding a 95-hole spinneret at  
30 60 metres per minute. The filaments emerging from the spinneret passed through a 2cm air gap into an aqueous spin bath containing 25% amine oxide. Amine oxide was leached from the filaments in the spin bath so that the cellulose was precipitated. The resulting tow of fibre was passed  
35 through a hot air chamber (100°C) to dry the fibre and was collected by winding. The tow produced was of 1.7 decitex per filament and contained 2.0% polyester based on cellulose. As seen by electron microscopy, the polyester was



present in the fibre as particles or domains elongated in the axial direction of the fibre. The polyester particles varied in length from 79 to 800nm and in diameter from 44 to 400nm. The particles generally had an aspect ratio of at least 1.5; most particles had an aspect ratio between 2 and 3.

The tow was crimped by passing through a stuffer box and then cut into 38mm staple fibre which could be carded on a No.5 Platt cotton card without addition of any lubricant, producing a strong coherent sliver. The sliver was drafted and spun into yarn on ring spinning machinery. A fabric knitted from the yarn had a soft handle and was dyed to a uniform medium red shading using "Serisol Fast Rubine BD 200" disperse dye.

#### Example 2

The procedure of Example 1 was repeated using 0.75% "Alftalat 03258" polyester based on cellulose. The staple fibre produced could be carded without addition of lubricant, as described in Example 1. The knitted fabric had a soft handle. The depth of shade achieved by disperse dyeing was low but was sufficient to act as a tracer, i.e. to distinguish it from other cellulose fibre by dyeing with disperse dyes. The tensile properties of the fibre were no different from those of standard lyocell fibre.

#### Example 3

The procedure of Example 1 was repeated using 0.25% "Alftalat 03258" polyester. The staple fibre produced could be carded without addition of lubricant, although more dust and fly was generated than with the fibres of Examples 1 and 2. The fibre, and yarn and fabric formed from it, had a harsher handle than the fibre of Examples 1 and 2 (similar to standard lyocell fibre without lubricant). The polyester still acted as a tracer which could be revealed by disperse

dyeing.

Example 4

5           Fibre was produced as described in Example 1 but using  
10.0% of the polyester.

10           The tow produced was cut into (5 mm) staple fibre. Cut  
fibre was placed at 0.3% concentration in water in a  
disintegrater for 100,000 revs. The Canadian standard  
freeness (CSF) of the fibre was then measured and fibres  
were examined by microscope. Paper hand-sheets were  
prepared from the disintegrated fibres and were tested using  
TAPPI standard paper testing equipment.

15           The results in Table 1 below show the properties of paper  
made from the fibre of Example 4 compared to those of paper  
made from bleached 1.7 dtex lyocell fibre prepared under  
similar conditions.

20

TABLE 1

	Biconstituent Fibre	Bleached Tencel
25 Bulk (cc/g)	3.06	3.56
Tensile Index (Nm/g)	20.8	1.7
Burst Index (MN/kg)	2.42	0.76
Tear Index (mNm <sup>2</sup> /g)	37.0	2.0
Air Resistance (secs)	2.5	
30 CSF (mls)	195	692

35           The low CSF of the disintegrated fibre indicates a high  
level of fibrillation. This was confirmed by microscopic  
examination which showed that fibre has a multitude of long  
thin fibrils. No evidence of cut fibre or detached fibrils  
was observed. The higher paper strength properties  
(tensile, burst and tear properties) of papers produced from  
the fibres of the invention are due to the high level of

fibrillation.

Example 5

5           It was noted during the spinning processes of Examples 1 to 4 that the back pressure during spinning was low compared to spinning standard lyocell fibres from a spinning solution having the same cellulose concentration.

10           In Example 5 the process of Example 1 was repeated but the ratio of wood pulp to amine oxide/water was changed in the initial mixing step and mixing under vacuum was continued until more water had been removed, resulting in a spinning solution containing 16.4% cellulose, 0.33% polyester, 74.9% amine oxide and 8.4% water. This solution  
15           could be successfully spun into fibre; the back pressure during spinning was similar to that during spinning of standard lyocell from a solution containing 15.0% cellulose.

20           The fibre of Example 5 could be cut into staple, carded, spun, knitted and dyed with the same results as described in Example 1.

Claims

1. Lyocell fibre, characterised in that the fibre contains elongated polyester domains of aspect ratio at least 1.5, the polyester domains being aligned substantially parallel to the axis of the fibre.

2. Fibre according to claim 1, characterised in that the polyester is a carboxy-functional polyester of acid value at least 10.

3. Fibre according to claim 1 or claim 2, characterised in that the fibre contains 3-60 wt% polyester based on cellulose and has an increased tendency to fibrillate compared to unmodified lyocell fibre.

4. Fibre according to claim 1 or claim 2, characterised in that the fibre contains 0.1-3 wt% polyester based on cellulose and has improved dimensional stability and crease resistance compared to unmodified lyocell fibre.

5. A process for the preparation of lyocell fibre or film by extruding a solution of cellulose in amine oxide through a spinneret or film die at elevated temperature via an air gap into an aqueous precipitation bath, characterised in that 0.1-60 wt% based on cellulose of a thermoplastic low-melting polymer is incorporated into the cellulose solution, the polymer having a melting point above 25°C but below the extrusion temperature of the cellulose solution.

6. A process according to claim 5, characterised in that the polymer has a melting point in the range 50-100°C.

7. A process according to claim 5 or claim 6, characterised in that the polymer is a polyester.

8. A process according to any of claims 5 to 7, characterised in that the polymer is a carboxy-functional

polymer of acid value at least 10.

9. A process according to any of claims 5 to 8, characterised in that the polymer has a branched structure.



Application No: GB 9707426.4  
Claims searched: 1-4

Examiner: Gavin Dale  
Date of search: 4 July 1997

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): B5B (BDB, BDF, BGA); C3M (MXC)

Int CI (Ed.6): D01D 5/28, 5/30, 5/32, 5/34, 5/36

Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	GB 1367378 (MONSANTO COMPANY) See claims 1, 3 and 7	1
A	EP 0046157 (AKZONA INCORPORATED) See page 11 lines 1-13	1

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.  
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A Document indicating technological background and/or state of the art.  
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